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Research activities supported by this grant focused on the following main topics: 1. Investigations of fluid flow through nanometer scale nozzles (nanojets), aiming at the development of miniaturized injectors in NEMS (Nano Electo Mechanical Systems). 2. Studies of the effects of surface roughness on the properties of confined fluids, pertaining to tribological and lubrication processes in nano-scale junctions. 3. Development of large-scale computer-based molecular dynamics simulations aimed at investigations of the effect of fluids (particularly water) on adhesive interactions in NEMS.

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MICROSCOPIC MODELING OF TRIBOCHEMICAL PROCESSES, VAPOR-PHASE LUBRICATION, AND NANOTRIBOLOGY IN MEMS

Grant Number: F49620 - 00 - 1 – 0149

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I. Summary of Research Activities

Research activities supported by this grant focused on the followingg main topics:

1. Investigations of fluid flow through nanometer scale nozzles (nanojets), aiming at the development of miniaturized injectors in NEMS (Nano Electo Mechanical Systems).

2. Studies of the effects of surface roughness on the properties of confined fluids, pertaining to tribological and lubrication processes in nano-scale junctions.

3. Development of large-scale computer-based molecular dynamics simulations aimed at investigations of the effect of fluids (particularly water) on adhesive interactions in NEMS.

1. Formation Stability and Breakup of Nanojets
Science 289, 1165-1169 (2000)
(Michael Moseler and Uzi Landman)

Liquid jets of macroscopic dimensions and their breakup into drops are ubiquitous phenomena which have been of scientific interest for at least three centuries, and which are utilized in venerable technologies such as fuel injection, cutting and machining , spraying and coating, fiber spinning, needle and syringe injection, ink-jet printing, and microelectronic and optoelectronic device manufacturing . With the importance of instabilities originating from perturbations at the nozzle opening and of surface tension as a driving force for capillary instabilities recognized already in the mid 19th century, the early stages of investigations into the nature of jets culminated in Lord Rayleigh's linear stability analysis over a century ago. However, since the full evolution of a jet is governed by the Navier-Stokes

(NS) equations, it is highly nonlinear thus preventing reliable analyses of the nonlinear dynamics close to breakup with linear stability methods or higher order perturbative treatments, requiring instead the development of a full nonlinear theory. Progress in this direction has been achieved via NS simulations and through analytical formulations based on the so-called lubrication theory. Particularly pertinent to our study are treatments based on the "slenderness approximation" allowing systematic derivation (starting from the NS equation) of viscous one-dimensional equations which can be solved numerically with relative ease (unlike the original three-dimensional NS equation). From a somewhat more practical perspective, significant efforts have been invested in studies addressing the design of (macroscopic) nozzles, including geometrical (e.g. nozzle shape) and materials (e.g. wettability of the nozzle by the fluid) factors.

In face of the relentlessly accelerating miniaturization of devices, as well as in light of fundamental problems pertaining to the dynamics of the jet close to breakup, that is when the jet diameter approaches the molecular size and the commonly used continuum fluid dynamics treatments are of questionable validity, we have initiated investigations of these issues through the use of large-scale atomistic molecular dynamics (MD) simulations. With such simulations we aim at extending our knowledge of jet processes to the nanometer-scale regime (i.e. nanojets, NJs). While such NJs are envisaged to impact most significantly various technologies (such as nanoscale materials' machining and patterning, printing of high-density miniaturized circuitry, and transfer of biological materials, e.g. genes, into cells with minimal damage), understanding the conditions for the formation of NJs and of their properties are most challenging. In particular, because of the reduced dimensions the behavior of such systems involves large spatio-

temporal variations and fluctuations of the liquid properties (such as temperature gradients and liquid density changes caused by viscous heating and evaporative cooling) complicating (and in many cases invalidating) the use of continuum mechanics treatments and requiring the development of physically reliable and accurate atomic-scale simulations.

In our studies we have shown, using propane as a fluid and gold for the nozzle material, that nanojets with diameters of several nanometers and with velocities up to 400 m/s, can indeed be created through high-pressure injection of the fluid through nanoscale convergent nozzles with heating or coating applied to the nozzle exterior surface to prevent formation of thick blocking films. Formation of such jets is accompanied by evaporative cooling processes and fast relaxation of the fluid velocity profile close to the nozzle exit. The atomistic description was related to, and integrated with, continuum hydrodynamic modeling through derivation of a stochastic lubrication equation that includes thermally triggered fluctuations whose influence on the dynamical evolution increases as the jet dimensions become smaller. A much sought for resolution of issues pertaining to the nature of the breakup and drop formation processes when the radius of the jet reduces to nanoscale molecular dimensions has been provided by us through comparative atomistic and hydrodynamic modeling, with a prediction of the emergence, close to the drop pinch-off point, of double-cone neck shapes deviating from the long-thread universal similarity solution obtained in the absence of such fluctuations.

2. Structures, Solvation Forces and Shear of Molecular Films in Rough Nano-Confinement

Tribology Letters, 9, 3-13 (2000),

(Jianping Gao, W. D. Luedtke, and Uzi Landman)

Molecular dynamics simulations of the tribological, rheological, and viscoelastic properties of confined films in equilibrium and under shear conditions, have been performed to date, almost exclusively, for atomically flat (smooth) crystalline confining solid boundaries. Shearing of fluids in confined (lubricated) junctions can be simulated (as well as studied in laboratory experiments) via attachment of a (horizontal) spring (of force constant k_s) to one of the confining solids (say the top one) with the free end of the spring translated with a constant velocity (v), or equivalently by attaching such springs to both of the confining solids and translating them in opposite directions with velocities v/2 and -v/2. For stiff springs (i.e., $k_s \rightarrow \infty$) the confining solid surfaces are set in motion at a relative constant velocity v with respect to each other, while for a finite k_s stick-slip phenomena may appear for $v < v_c$ where v_c is a critical velocity above which a transition to steady motion occurs.

However, at shear rates of interest in modern tribological systems (lubricated films of the order of 1 to 2 nanometers with sliding velocities of ~ 1-10 m/s, i.e. shear rates of 10^9 to 10^{10} s^{-1}), it is commonly found in simulations employing flat close-packed (atomically structured) solid surfaces, that for large k_s and for chain molecules (as well as spherical molecules whose size (diameter) is incommensurate with the interatomic distance in the confining solid surfaces) the motion of the surfaces is accompanied by slip of the confined film at the film-solid interface. In this study we have shown through large-scale molecular dynamics simulations, that when the confining solid surfaces are rough such boundary-slip of the confined film (n-hexadecane) is highly suppressed even for rough surface

morphologies characterized by atomic-scale height variations. Furthermore, our investigations revealed remarkable sensitivity of the structural, dynamic and rheological properties of confined molecular films to the surface morphology, both under static conditions (that is when the solid boundaries are stationary) and under shear (that is when the solid boundaries are in relative motion with respect to each other), resulting from frustration of ordering in the molecular film in rough surface confinements.

In our current studies we explored through the use of large–scale grand-canonical molecular dynamics simulations surface roughness effects on the structure, dynamics and rheology of a molecular fluid (hexadecane) confined between solid (gold) surfaces. These investigations revealed a remarkable sensitivity of structural, dynamic and rheological properties of the molecular films to the confining surface morphology. Indeed, our simulations demonstrated that even a surface roughness characterized by atomic – scale height variations can modify in a most significant way the nature of fluid films confined between such surfaces, both under static conditions (i.e. when the solid boundaries are stationary) and under shear (i.e. when the solid boundaries are in relative motion with repect to each other).

For the static case the reduced ordering propensity of the rough-surface confined film (compared to that of the film confined under similar conditions by flat solid surfaces) is exhibited by significant inhibition of the development of density- layered (stratified) structures in the film, with consequent strong suppression of the development of solvation forces, the disappearance of solvation force oscillations, and the emergence of liquid-like dynamic and response characteristics (that is, higher molecular mobilities, and continuous expulsion of molecules from the confined region

6

in response to reduction of the gap-width). The different nature of the molecular films in the flat and rough surface confinements is portrayed also in the characteristics of the free volumes calculated for the two systems, with that for the flat surface confinement exhibiting local minima at gap-widths corresponding to well – layered film configurations, while in the rough surface confinement the free volume decreases with the gap-width in a smooth monotonic manner; overall the free volume is larger in the rough surface confinement than in the flat surface one, except in the vicinity of gap-widths corresponding to intermediate configurations between well – layered states of the film in the flat surface confinement.

When the rough-surface boundaries are set in motion (at a high shear rate) the above characteristics of the confined film maintain, with the interfacial layer of the film sticking to the adjacent solid boundaries (on the two sides of the confinement gap), resulting in partial slip inside the film and development of shear stress in the viscous molecular fluid (unlike the case of flat boundaries where the confined film slips at the solid boundaries resulting in a vanishingly small shear stress in the film). The effective viscosities calculated for the film in the rough surface confinement are found to depend exponentially on the reciprocal of the (per molecular segment) free volume in the confinement.

Analysis of our results shows that one of the main effects of the rough surface morphology on the properties of the confined films is the frustration of ordering in the film. This observation, and its apparent relation to the principle of frustration of ordering that underlies our recently proposed method for friction control in lubricated junctions through externally applied small amplitude oscillations of the gap-width, suggests that morphological

patterning of surfaces could provide ways for controlled modifications of frictional processes in thin-film lubricated nanotribological systems.

The above results are of importance for understanding the behaviour of lubricating films under high confinement conditions, and they allow investigations (both molecular dynamics simulations and experimental studies) of thin-film tribology and rheology at extremely high shear rates that are of relevance to current technologies. Additionally, the results obtained in our simulations for the dynamics and rheology of fluid films sheared between rough boundaries are of interest for studies pertaining to the effect of roughness on the boundary conditions used in the context of hydrodynamical approaches to such film-flow problems, including roughness effects on the effective slip – length.

3. Molecular Dynamics Simulations of Thin- Water Films Confined by α-quartz Crystalline Surfaces

3.1 Model and Simulation Method

The water model used in our simulation is the SPC/E model [the extended simple point charge model, Berendsen, H.J.C., Grigera, J. R., and Straatsma, T. P., *J. Phys. Chem.*, **97**, 6269(1987)]. This model consists of three partial charges. The two positive charges (+0.4238e) are positioned at the centers of the two hydrogen atoms and the one negative charge is positioned at the center of the oxygen atom. The O-H bonds are fixed at 1.0 Å and the HOH angle is fixed at 109.47°.

To relate to the situation pertinent to NEMS (and MEMS) and to study the tribological properties of thin-water films, the above water model is used in conjunction with silica solid surfaces. In particular, α-quartz crystalline

solids are built using the Crystal Builder module in Cerius2 by Molecular Simulation Inc. After the α-quartz crystalline solids are built, they are rotated to expose the (1, 0, -1) surface. Two different surface models are employed in the simulations to study the effect of surface wetting properties on the confined thin-film water. The first one is just the α-quartz (1, 0, -1) surface consisting of silicon atoms and oxygen atoms. The interactions between these atoms and the water molecules are modeled by the normal Lennard-Jones potential only. The second surface model is based on the first one, but surface hydroxylated by adding hydrogen atoms to the surface oxygen atoms, with the SiOH angle equal to the HOH angle in the water model. In addition, partial charges are added at the positions of surface silicon atoms and oxygen atoms as well as the surface hydrogen atoms. The negative charges at surface oxygen atoms are balanced by the positive charges at surface silicon atoms and surface hydrogen atoms, so the whole surface remains neutral at further distance. During the simulations, the surface silicon and oxygen atoms in both models are fixed at their crystalline lattice sites while the surface hydrogen atoms are allowed to move with fixed bond length and bond angle (that is, they are allowed to "rotate"). The surface potential parameters are the same as used by Wensink, *et al* . [Wensink, E.J.W., Hoffmann, A. C., Apol, M. E. F., and Berendsen, H.J.C., *Langmuir*, **16**, 7392(2000)].

Our simulations use the Verlet algorithm with RATTLE [Andersen, H. C., *J. Comp.Phys.*, **52**, 24(1983)], for bond and angle constraints. The time step is 3 femto-seconds. The parallel molecular dynamics programs used in our previous simulations of confined fluids are based on space decomposition method that is suitable for systems with a very large number of molecules

and short range atomic interactions. Since water simulations include long range Coulomb interaction between all charges in the model system, it is not practical to model hundreds of thousands of water molecules for sufficient long time period to obtain statistically meaningful results. In order to perform such simulations efficiently in a massive parallel computer environment, we redeveloped our programs using a **force decomposition method**. After many careful "tuning experiments", the method performs currently very well. For a systems with 2000 water molecules and 21840 solid atoms (9360 point charges), the program performance scales to about 30 CPUs with reasonable efficiency. This program allows us to model such a large water system and to extend each run for half million to one million time steps in a reasonable amount of wall clock time. In the simulations described below the surface size in the x-y plane is 96.2 X 98.2 Å, and the thickness of each substrate is approximately 12 Å.

3.2 Sample Results

(i) Wetting angle

The simulated model system consists here of a water droplet of 2000 molecules and a single α-quartz substrate with (1, 0, -1) surface exposed to water. Periodic boundary conditions for the substrate are imposed in both x and y directions that are parallel to the surface. No periodic boundary conditions are imposed on the water droplet so that the droplet does not interact with its own images. However, the periodic boundary conditions for the substrate allow the droplet to interact with an extended solid surface with no edges or boundaries, as desired. At the beginning of the simulation, the droplet is positioned to be just at contact with the solid surface. Two simulations are performed to compare the wetting properties of the unhydroxylated quartz surface with those of the hydroxylated one. On the

unhydroxylated surface, after the droplet equilibrates for about 3.6 ns (> 1 million steps), the shape of the droplet remains as a half sphere with a contact angle close to 90° (see Fig.1). On the other hand, On the hydroxylated surface, the water droplet spreads at a pretty fast rate—that is this surface is wetted by water (see Fig. 2).
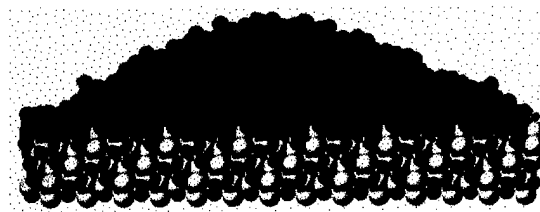
Water droplet on α-quartz surface
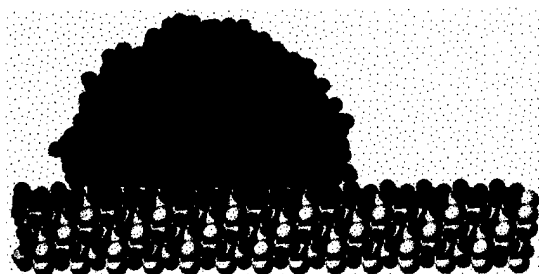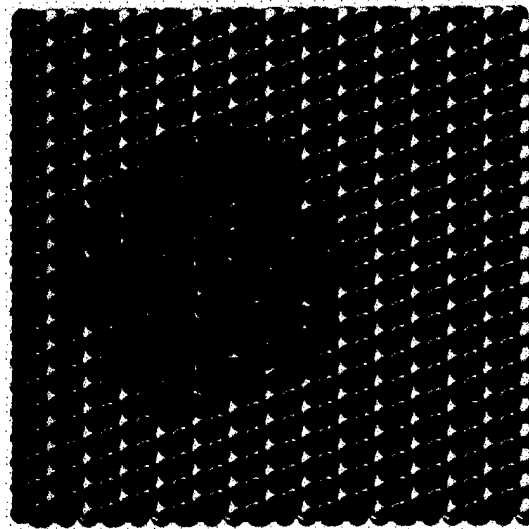

Side view of droplet after 3.6 ns MD equilibration
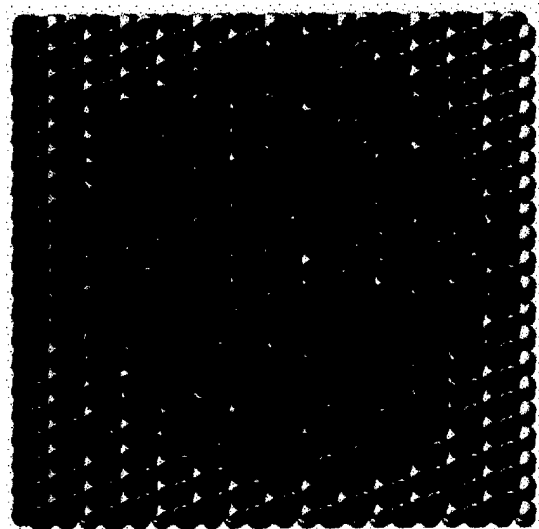
Bottom water layer viewed from top

Fig 1

Water droplet on hydroxylated α-quartz

Side view of droplet after 420 ps MD equilibration

Bottom water layer viewed from top

Fig 2

ii) Water bridge between hydroxylated surfaces

The simulated model system consists here of a water droplet of 2000 molecules positioned between two α-quartz substrates with the (1, 0, -1) surfaces exposed. The surfaces are hydroxylated as described above. The top substrate is free to move under the influence of the total interaction force between the water droplet and itself. The external force on the top substrate is set to zero. This simulation (and the one described in (iii)) aim at exploring the nature of the capillary interfacial forces acting during water condensation (or drying) at ultra-narrow junctions in NEMS.

The periodic boundary conditions used here are of the same type as described under (i), so the water droplet has no images to interact with. At the beginning of the simulation, the droplet is just at contact with the solid surfaces. Once the dynamics begins, the top substrate is pulled downward by the water droplet rapidly, and it continues to squeeze the droplet into a thin film. This process gradually slows down as the thickness of the interfacial film approaches about 2 to 3 water molecule diameters. This behavior is different from that found for organic lubricants. When other organic lubricants (globular, e.g. OMCTS, or chain-like, e.g. alkanes) are confined by atomically smooth surfaces into thin films, well-ordered atomic layers form as the film thickness approach 4-5 molecular sizes. For such films the solvation force (the force acting in the normal direction to the confining surfaces) oscillates between attractive and repulsive values and the free pulling the top substrate will stop as the first repulsive solvation force appears. This is not the case here, where the spreading droplet pulls the two confining surfaces together, all the way down to a water film thickness of 2 to 3 water molecule diameters (see Fig. 3).

Water droplet pulling down the free top substrate
equal time interval of 60 ps between configurations
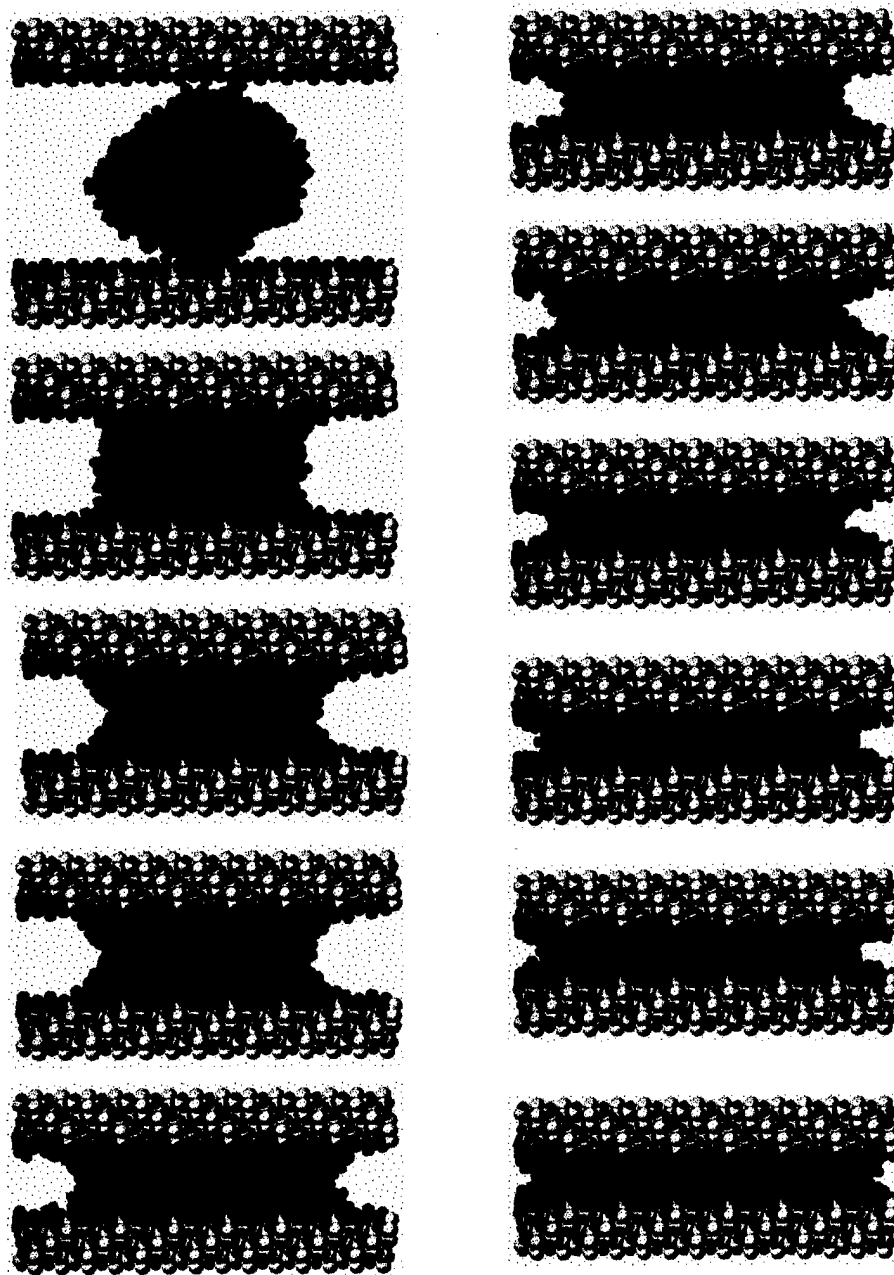(from top left to bottom right)

Fig 3

iii) **Water bridge between unhydroxylated surfaces**

In this set of simulations, we study a finite water thin film confined by two unhydroxylated surfaces, for selected values of the gap size (film thickness). The same type of periodic boundary conditions as those described above are employed, so that the water film has no images to interact with. The finite size of the thin film allows continuous variation of the film thickness. At each selected gap size, the water film is equilibrated for 1 to 3 nanoseconds; the equilibrium values of the density profile and solvation force are computed for the last few hundred picoseconds.

The density profile (Fig. 4) shows now clear oscillations for film thicknesses smaller than 14 Å (3 layers). The peaks are much more extended in this case as compared with the density profiles obtained by us previously from simulations of confined simple molecules and small alkanes. This indicates that no well-ordered water layers have been formed, even for film thicknesses of less than 3 molecular sizes. In the Fig. 5, the solvation force is plotted against the film thickness. As seen, when the film thickness is greater than 3 molecular sizes, the solvation force is slightly negative (attractive), and it shows almost no oscillation until the film thickness becomes less than 3 molecular sizes. Generally, the only noticeable feature in the solvation curve is the rapidly increasing repulsive portion for a film thickness less than 8 Å. This is due to squeeze of two boundary water layers against each other.
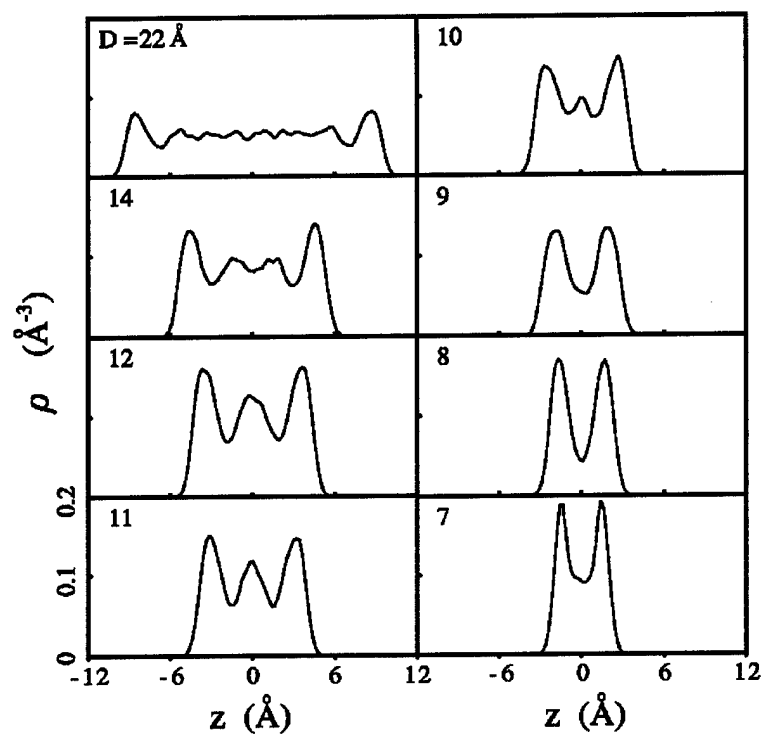
density profile of confined water droplet T=300K

Fig 4
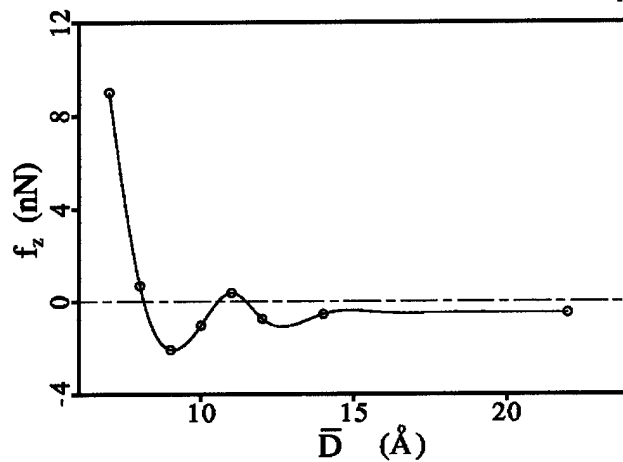
solvation force of confined water droplet

Fig 5

4. Adhesive Interactions in NEMS

Aiming at simulations of the effects of capillary condensation on adhesive interactions pertaining to nanometer scale contacts, with an application to the operation of NEMS devices, we have invested efforts in developing a molecular dynamics code specifically constructed for such investigations, as well as in developing the interaction potentials to be used in these large-scale simulations.

Molecular dynamics simulation of water stiction in MEMS

The importance of thin water films on the friction of MEMS has been known in the literature. One of the focuses is to understand the capillary forces and stiction forces caused by nano-scale thin water films in MEMS and NEMS. In this study, we performed MD simulations to explore the structural and dynamical properties of thin water films absorbed on the silica surfaces. The capillary forces and friction forces of a silica tip in contact with the thin water film are computed in the simulations.

4.1 Model

Developing accurate model potentials of silicon dioxide for computer simulations has been an active research field for the past decade. After extensive search through the literature, we have chosen BKS model[1] potential for simulating silica. It was developed for bulk silica with *ab initio* methods and it has been used in the simulations of amorphous silica surfaces by Binder's group recently[2]. The BKS potential has three terms:

$$u(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6},$$

The first term is the normal Coulomb interaction between all effective charges of silicon and oxygen ions, the exponential term represents a short range repulsion and the last term is a van der Waals attraction. The latter two terms only act between silicon-oxygen and oxygen-oxygen atomic pairs. The effective charges for the ions are q_{si} = 2.4e and q_o = -1.2e. In our simulations, the Coulomb interaction is treated as a very long range potential and is truncated at 30Å with a short-range switched shift function[3]. The water model used in this study is the extended simple point charge potential (SPC/E)[4]. Mixing rules are used for water-silica interactions in BKS potential form. (following Bakaev and Steele[5]) The other short range potentials are cut off at 12Å.

We first performed MD simulations of BKS model silica to create the amorphous silica surfaces used in the subsequent studies. The initial configuration is a crystalline quartz slab with two open parallel surfaces and periodic boundary conditions in x and y directions. It is heated to above the melting point in MD simulations, and is equilibrated at 5200K for a hundred thousand steps. Then it is cooled down at a computationally slow rate to the room temperature, 300K. The result is an amorphous silica slab with two rough surfaces. This system contains 4992 silicon atoms and 9984 oxygen atoms and has a lateral dimension of 82.5Å by 78.6Å. The thickness of the silica slab is about 30Å. Figure 1 shows a snap shot of the amorphous silica slab.

17

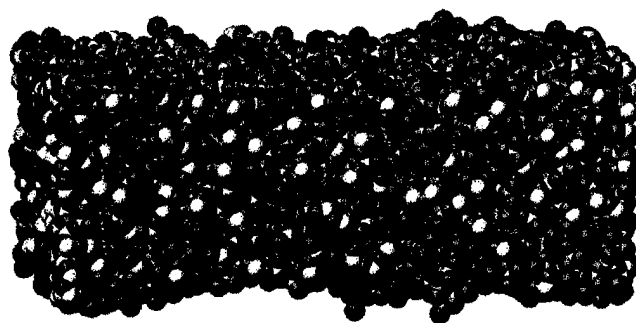Amorphous SiO$_2$ surface

Figure 1

A water layer of 3000 molecules are then added on to one of the amorphous silica surface. After the whole system is equilibrated at 300K, the absorbed water layer is about 10Å thick. Figure 2 shows a side view of the thin water layer absorbed on the silica surface.

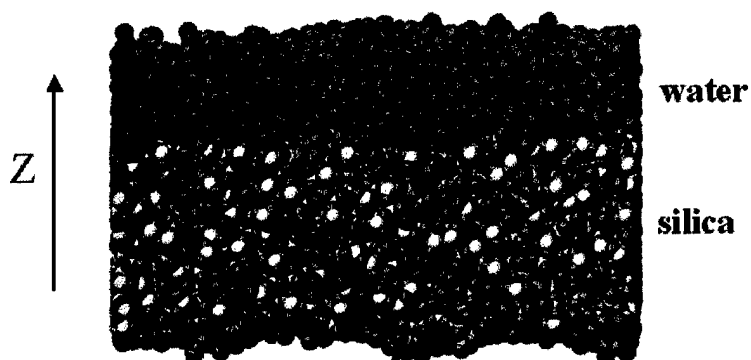**Thin water film on rough silica surface**

Figure 2

4.2 Code development

We have developed a fully parallelized new code for this project. Our programs for simulating organic confined lubricants use the space

decomposition method due to its benefit for larger systems with short range interactions. In this project, we find the optimal algorithm for the parallel computation of charged particle systems is to use force decomposition. The scaling properties for this system are pretty good up to 24 processors. This is the number of the processors we used for most of our simulations. The simulated systems usually consist 25000 to 30000 charged atoms. A typical run of 100,000 steps, corresponding to 300 ps, lasts for about 100 hours wall clock time with 24 dedicated computer processors.

4.3 Results

a) Thin water film in equilibrium.

The averaged density profiles of solid atoms and water molecules perpendicular to the surfaces (z direction) are plotted in figure 3. Note that the overlap of the two density profile provides an estimate of the roughness of the solid surface. We do not see any layering structure in the water profile. It can also be observed that the thickness of the water film is about 10 angstroms.
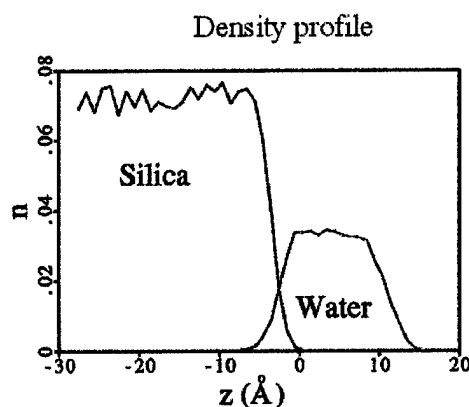

Density profile

Figure 3

One of the first questions to be asked for this system is that does the thin water film freeze at room temperature when it is absorbed on a silica surface. In order to examine the fluidity of the absorbed water film, we plotted the mean squared displacements of water molecules in the absorbed film. The thin film is divided into two regions, boundary region (the overlap region in the density profiles) and non-boundary region. In figure 4, the green line shows that the diffusion rate of the boundary water molecules is only reduced by a factor of 2 from the others. The calculated diffusion coefficient is 0.11 Å^2/ps ($10^{-4}\text{cm}^2\text{•s}^{-1}$) for the molecules in the film and is 0.06 Å^2/ps ($10^{-4}\text{cm}^2\text{•s}^{-1}$) for the boundary molecules. As a comparison, the experiment value for bulk water (25°C) is 0.23 $10^{-4}\text{cm}^2\text{•s}^{-1}$. Apparently the film did not freeze and the molecules diffuse like in the liquid.

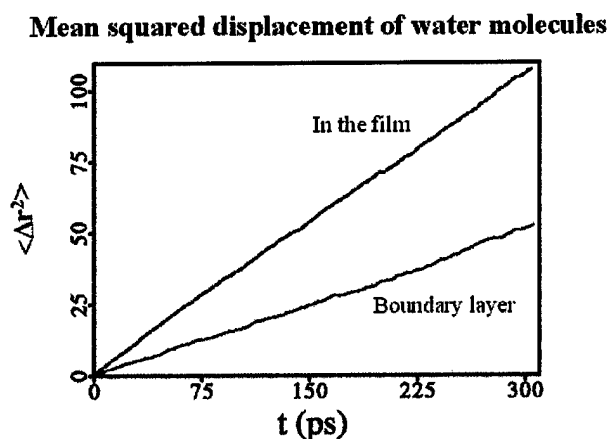**Mean squared displacement of water molecules**

Figure 4

b) Thin water film between a silica tip and a silica surface.

To model a cantilever system, a tip with a 30Å radius is carved out from the amorphous silica with the ratio between the number of silicon and oxygen

remaining one half so the net electric charge for the tip is zero. The spherical surface of the tip is then equilibrated by MD simulation at 300K. After the equilibration, the tip is introduced from the top of thin water film. While the tip is slowly moving down towards the water surface, some of the water molecules jump into contact to form a liquid bridge. In figure 5, we show that when the tip is stopped above the water surface at Z_{min} = 20.5Å (Z_{min} is measured from the highest point of the solid surface to the lowest point of the tip), the water molecules continue to move up towards the tip. The three pictures in Figure 5 represent snap shots at different time during the simulation.
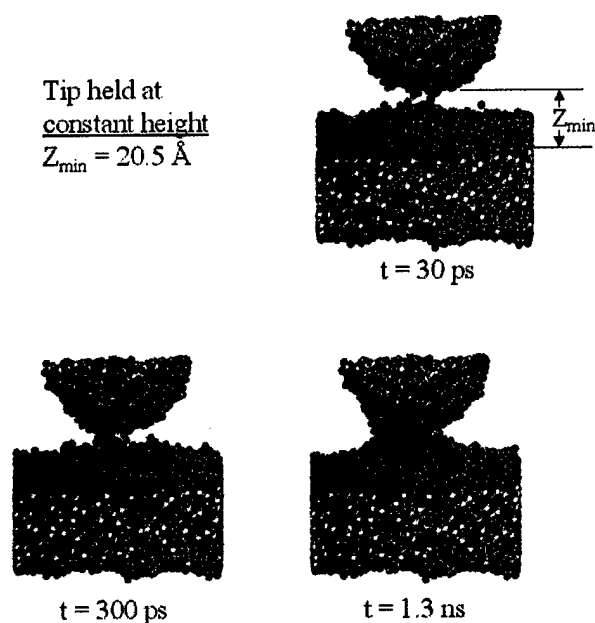

Figure 5

The force imposed by water molecules on the tip is plotted in Figure 6 as a function of time during the formation of the liquid bridge. The absolute value of the force does not grow as the liquid bridge grows.

Capillary force on the tip at $Z_{min} = 20.5$ Å

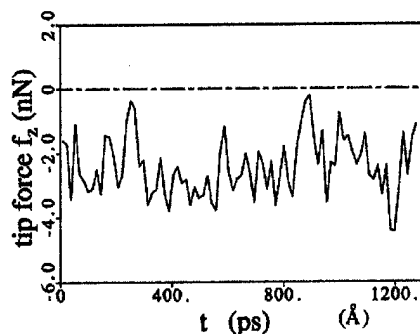tip force f_z (nN)

t (ps) (Å)

Figure 6

To further probe the fluidity of the absorbed water film, the tip is pushed down at a constant load into the water film during MD simulations. Figure 7 shows the bottom position of the tip, Z_{min}, as a function of time for two simulations with external load on the tip, f_L, equals to 2 nN and 10 nN respectively. Both curves show that the processes of the tip approaching the substrate are relatively smooth, no stepwise behavior is displayed. This indicates that the water underneath the tip is squeezed out smoothly. The tip moves faster with the bigger load. In the case of $f_L = 10$ nN, the tip was able to reach the substrate surface during the simulation. These simulations reveal that there is no layering structure or frozen structure formed in the water confined between the tip and the substrate.
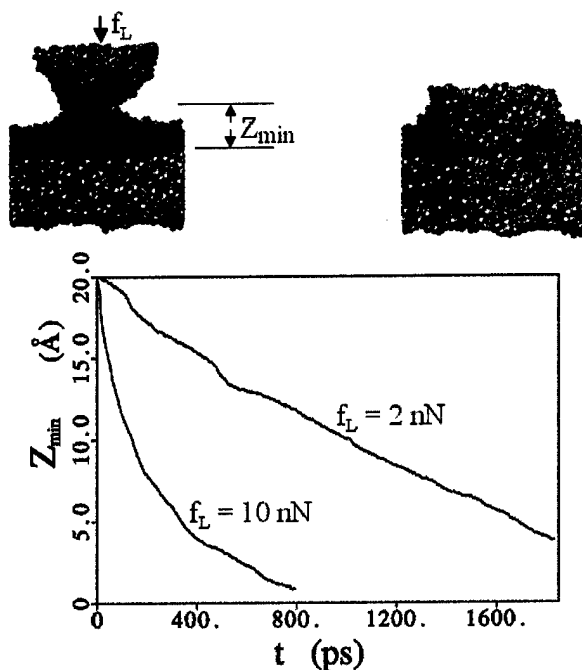
22

Figure 7

In Figure 8, we plot the capillary force between the tip and the substrate as a function of the tip height, Z_{min}. In these simulations, the tip position is kept constant at each given value of Z_{min} until the force on the tip by the water film reaches a plateau. Then the average value of the force is computed from the plateau. For most values of Z_{min}, the force does vary significantly. In contrast to the thin film organic lubricant confined between atomically smooth surfaces, there is no oscillatory behavior in this force. Note that the water surface is approximately at $Z_{min} = 10\text{Å}$. The first noticeable variation of the capillary force is when the bottom of the tip goes through the water surface. The force remains mostly attractive as the tip goes deep into the water until it is very close the substrate. It means the adhesive force caused by the absorbed water film will pull the tip directly to the substrate. The peak at $Z_{min} = 3\text{Å}$ indicates that some water molecules are trapped underneath the tip when the tip gets so close to the substrate.
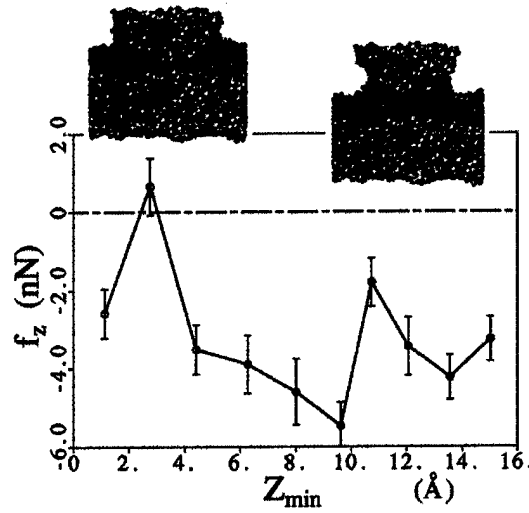
23

Figure 8

c) Tip sliding through the water film.

In the frictional simulations, the tip is moved at a constant velocity $V_s = 10$ m/s parallel to the substrate surface with constant height. The shear force and the normal force exerted on the tip by the water film are recorded as a function of the time. In figure 9, the shear force (top panel) and normal force (bottom panel) are plotted for $Z_{min} = 5.8$ Å. At this height, the tip is partially immersed in the water film. Note that the shear force (~15 nN) is very large. The estimated mean shear stress is 1.2 GPa. The mean shear force is computed for the latter part of the process which corresponds to a steady state. It is also noted that during the steady state, the normal force remains attractive, meaning the tip is still subject to a pulling force from the water film.
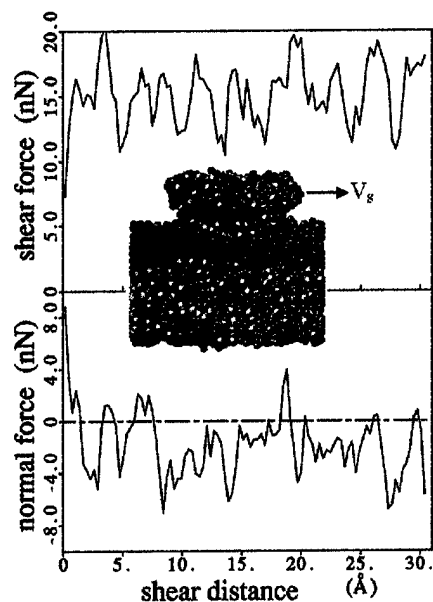
24

Figure 9

Figure 10 is the same plot for the tip height raised to $Z_{min} = 8.3$ Å. It is interesting to note that the shear force only decreases slightly when the thickness of the confined water underneath the tip increases by 2.5Å which reduces the shear rate in the water film. It means that the main contribution to the shear force may not due to the water viscosity.
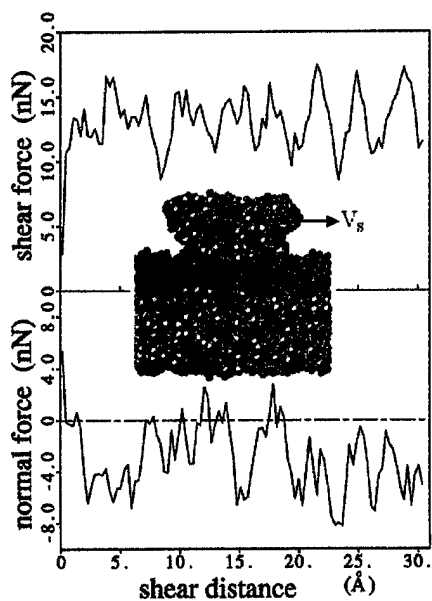

Figure 10

25

d) The effect of tip wetting properties.

The insets in Figure 9 and 10 show the side views of the tip scratching the water film surface. The both pictures clearly display the contact between the rough surface of the tip and the water film, as well as the partial immersion of the tip into the water film. In order to find where the slip takes place during the tip motion and to find the effect of the tip wetting properties on the shear force and slip interface, we changed the values of effective charges of silicon and oxygen atoms in the tip, but leave the substrate unchanged. When the charge values are reduced to 1/3 of the original values, the shear stress reduces sharply, while the normal force becomes slightly positive, meaning the tip surface becomes much less wetting. Figure 11 shows the force comparisons for the cases of the normal tip and the reduced charge tip with $Z_{min} = 5.8$ Å. Note that the shear force for the reduced charge tip is only about one fifth of that of the normal tip. In figure 12, the mean displacements of water molecules in contact with the tip for the same simulation as in Figure 11 are plotted. The top panel is for the normal tip and the bottom panel is for reduced charge tip. The black lines show the displacement of the tip and the other colored curves correspond to different cutoff distances between the molecules and tip atoms. These numbers effectively define the water layer thickness for choosing the water molecules near the tip surface. The colored curve closest to the black line in the top panel represents the smallest cutoff value, i.e. thinnest boundary layer near the tip surface. The cutoff values are listed in the bottom panel. As seen clearly in the figure, for the normal tip, very little slip occurs at the interface between the tip and the water. While for the reduced charge tip (non

wetting), almost total slip takes place even though the tip is still partially pushed into the water surface.
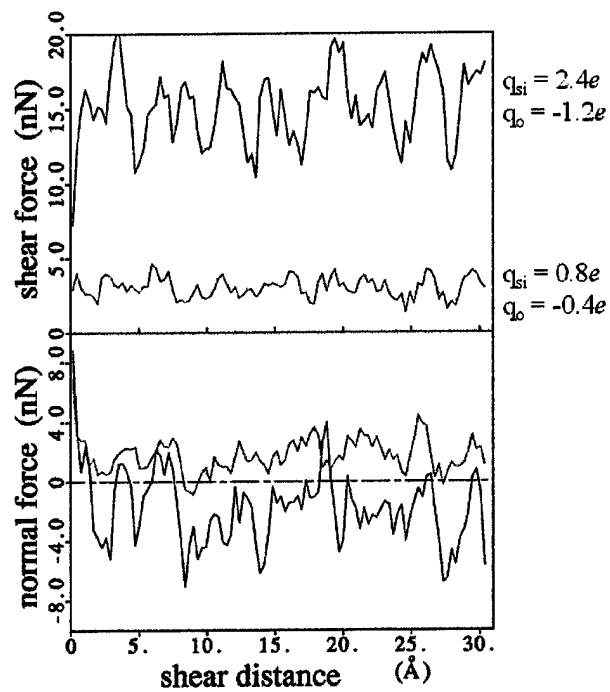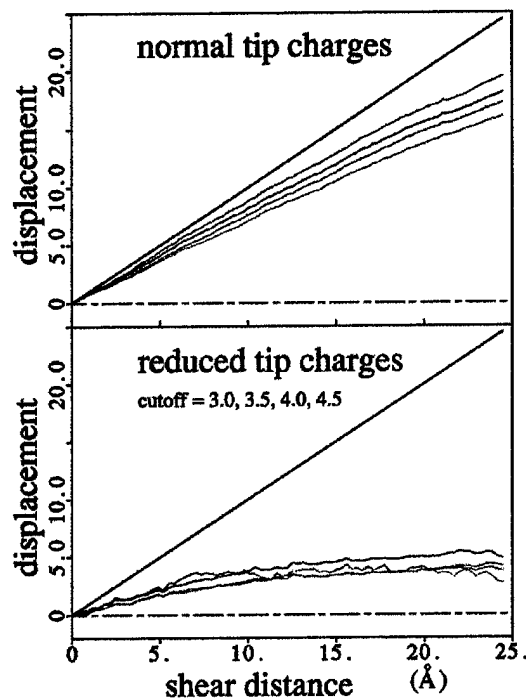

Figure 11

Figure 12

Figure 13 and 14 are corresponding plots for the shear forces and the mean molecule displacements comparisons when the tip height is raised to $Z_{min} =$ 8.3 Å. The same sharp reduction of shear force is observed for reduced effective charges in the tip.
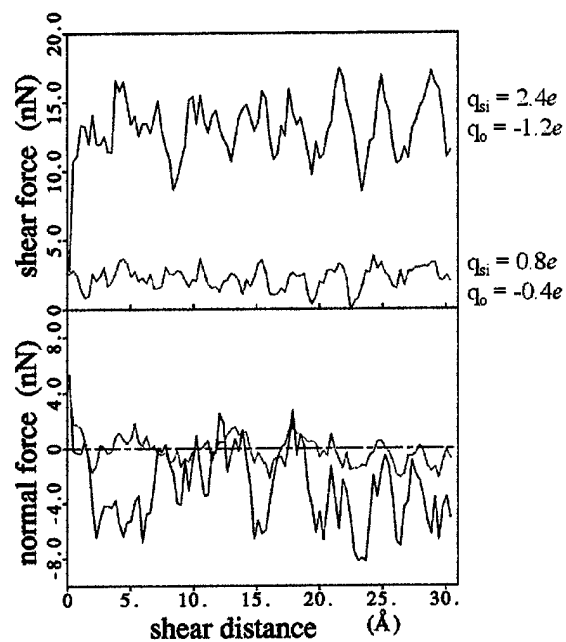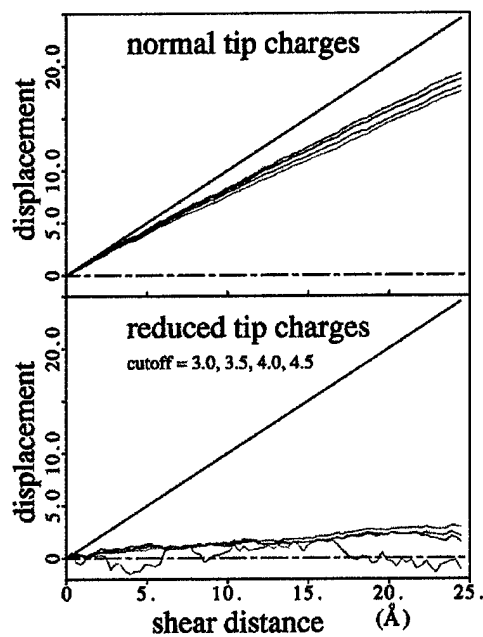
28

Figure 13

Figure 14

The following table lists the effect of the wetting properties of tip surface on the shear force

tip charges Z_{min}	Normal charges Strong wetting	Reduced charges Less wetting
5.8Å	15.84 nN	3.02 nN
8.3Å	13.22 nN	2.29 nN

4.4 Summary

One nanometer thick water film remains fluid when absorbed on silica surfaces at the room temperature. No ordered structure is found when a tip pushed down into the water film. Strong capillary forces is observed when tip moved close to the water film. Strong shear resistance is measured when tip is in contact with the water film. Finally, the shear resistance (water stiction) becomes significantly small when the wetting strength of the tip surface is reduced.

1. B.W.H. van Beest, G.J. Kramer and R.A. van Santen, *Phys. Rev. Lett.* **64**, 1955(1990).

2. A. Roder, W. Kob and K. Binder, *J. Chem. Phys.* **114**, 7602(2001).

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II. Major Accomplishments

1. Development of a unique molecular dynamics program for simulations of nanojets.

2. Development of design principles for creation of liquid (propane) nanojets via pressurized injection through a metallic convergent nozzle, coated by a nonwetting material to prevent blocking due to condensation of films on the outer nozzle surfaces. Such nanojets are expected to impact various technologies, such as miniaturized fuel injectors, nanoscale machining and patterning, printing of miniaturized high-density electric circuitry, and transfer of biological materials (e.g. genes and drugs) into cells.

3. Derivation of modified lubrication equations that include size-dependent stress fluctuations. The modified equations were tested against the atomistic simulations and were shown to yield a remarkable agreement. The main significance of this achievement is that it extends the hydrodynamic treatment of jets to the nanometer scale regime. This could have great importance in the design and fabrication of NEMS devices.

4. The first MD simulation of nano-scale lubricant film confined by atomically rough surfaces. These investigations revealed a remarkable sensitivity of structural, dynamic and rheological properties of the molecular films to the confining surface morphology. Indeed, our simulations demonstrate that even a surface roughness characterized by atomic – scale height variations can modify in a most significant way the nature of fluid

31

films confined between such surfaces, both under static conditions (i.e. when the solid boundaries are stationary) and under shear (i.e. when the solid boundaries are in relative motion with respect to each other). These results are of importance for understanding the behavior of lubricating films under high confinement conditions, and they allow investigations (both molecular dynamics simulations and experimental studies) of thin-film tribology and rheology at extremely high shear rates that are of relevance to current technologies.

5. The properties of thin water films between a silica tip and a silica substrate are studied by MD simulations. This study provides a powerful tool to investigate the capillary forces and stiction forces caused by nano-scale thin water films in MEMS and NEMS. A fully specialized parallel computer program is developed for this study. Model amorphous silica substrates and silica tips are generated by separate MD simulations. The forces induced by the thin water films between the tip and the substrate are computed for varies conditions. They include forming a capillary bridge between the tip and the substrate and sliding the tip through the thin water films at different distances from the substrate. The simulations reveal that the water film does not freeze when absorbed on an amorphous silica surface or confined between a silica tip and a silica substrate, but it displays a significant resistant force to the tip sliding. In addition, this sliding (friction) force due to the thin water film strongly depends on the wet property of the tip surface. Changing the tip surface from wetting to slightly non-wetting significantly reduces the sliding force on the tip.

6. MD simulations and analysis of the microscopic origins of Amonton's law.

Amontons' Law states that for any two materials the (lateral) friction force is directly proportional to the (normal) applied load, with a constant of proportionality – the friction coefficient – that is constant and independent of the contact area, the surface roughness and the sliding velocity. No theory has yet satisfactorily explained this surprisingly general law, all attempts being model or system dependent. We performed extensive simulations of hexadecane thin films (about 1nm in width) confined between atomically rough solid surfaces. The results of these simulations are in general agreement with recent and past experiments, and with Amontons' Law, and show that the local energy-dissipating mechanisms are not 'mechanical', as assumed in most models, but 'thermodynamic' – like miniature irreversible Carnot engines that cycle between compression and expansion as the surface asperities of two sliding surfaces pass over each other.

An interesting feature of the MD analysis is that for such dynamic, non-equilibrium, energy-dissipating processes, the Weibull distribution serves a similar purpose as the Boltzmann distribution for classical systems at equilibrium. Another interesting conclusion is that the concept of the 'area of contact' is an undefined, not-fundamental and unnecessary quantity, whether at the nano-, micro- or macro-scales. However, it may serve as a convenient phenomenological parameter for describing the really fundamental parameters, which are the number of atoms, molecules or bonds involved in an adhesive or frictional interaction

III. Technology Transitions

The research achievements resulting from work supported by this grant have been the subject of significant coverage by News and Technological publications. These include:

1. An article in <u>Science News</u> , August 19, 2000 issue (Volume 158, page 118).

2. <u>Nanotech Alert</u>, published by John Wiley Inc New York, NY – August 18, 2000.

3. <u>National Geographic.com</u> – August 18, 2000.

4. An article in <u>Technology Research News</u> (September 2000).

5. A description of our work appeared in Popular Mechanics (article on "Micro Warfare", February 2001, page 62).

In December 2000, Uzi Landman gave a seminar at the Materials Laboratory of the Wright-Patterson Air Force Base,in Dayton, Ohio. This provided an opportunity for discussions on scientific issues of joint interest.

IV. Supported Personnel

Dr. Jianping Gao, Senior Research Scientist – 51%
Dr. Charles Cleveland, Senior Research Scientist – 14%
Dr. Robert Barnett, Senior Research Scientist – 9%
Dr. W.D. Luedtke, Senior Research Scientist –4%

V. Publications and Presentations

Publications

" Formation, Stability, and Breakup of Nanojets", M. Moseler and U. Landman, Science **289**, 1165 (2000). <u>Cover of the August 18 issue.</u>

"Structures, Solvation Forces and Shear of Molecular Films in a Rough Nano-Confinement", J. Gao, W. D. Luedtke and U. Landman, Tribology Letters **9**, 3 (2000).

"Nanoscale Lubrication and Friction Control", in "Nonequilibrium Dynamic

Processes at with J. Gao and W.D. Luedtke, in "Fundamental of and Bridging the Gap Between Macro- and Micro/Nanoscale Tribology" Ed. B Bhushan (Kluwer, Dordrect, 2001), pp. 607-629.

"On the Effect of Roughness on Structures, Solavation Forces and Shear of Molecular Films in a Nano-Confinement", with J.Gao and W.D. Luedtke, in "Fundamental of and Bridging the Gap Between Macro- and Micro/Nanoscale Tribology" Ed. B Bhushan (Kluwer, Dordrect, 2001), pp. 583-605.

"Frictional forces and Amontons' law: from the molecular to the macroscopic scale", Jianping Gao, W. D. Luedtke, D. Gourdon, M. Ruths, J. N. Israelachvili, and Uzi Landman, in preparation.

Invited Talks

Uzi Landman

Invited Speaker, Symposium on "Large-Scale Computations in the Simulations of Materials", Carnegie-Mellon Univ., Pittsburg, March 2000.

Invited Speaker, "International Conference on Nanotribology: Theory, Experiment, Applications", Ubud, Bali, April 2000.

Invited Speaker in ASM International Educational Symposium 2000 on "Nanomaterials and Nanotechnology Challenges for the New Millenium: Shaping the World Atom by Atom", Oak Ridge, May 2000.

Invited Lecturer (3 lectures) at NATO ASI on "Fundamentals of and Bridging the Gap Between Macro- and Micro/Nanoscale Tribology", Hungary, August 2000.

Keynote speaker 1st Georgia Tech Conference on Nanoscience and Nanotechnology, October, 2000.

Invited speaker Materials Laboratory, Wright-Patterson Air Force base, December, 2000.

35

Invited speaker, Special Symposium on Nanoscience and Technology, AAAS Annual Meeting, San Francisco, February, 2001.

Invited speaker, Sackler Symposium of the US National Academy of Science, on Nanoscience, Washington DC, May, 2001.

Plenary Speaker, Nano-7/Ecoss-21, Malmo, Sweden, June, 2002.

Plenary Speaker, Asia SPM4 and Taipei Symposium on Nanotechnology, Taipe, Taiwan, August, 2002

Invited Speaker. Gordon Research Conference on Tribology, Roger Williams University, Bristol, LI, August, 2002.
Plenary speaker, APS Computational Physics Conference, San Diego, August, 2002.

Key note lecturer, 1st ESF-Nanotribology Workshop, Portovenere (La Spezia), Italy, October, 2002.

Invited Speaker, EUCHEM Conference on Molecular Tribology, Stockholm, Sweden, December, 2002.

Invited Speaker, Adhesion Society Meeting, Myrtle Beach SC, February, 2003.

Jianping Gao

Invited Speaker in CECAM - SIMU Workshop on "Simulation and Theory

of Solid Friction: From Atomic Shear Forces to Macroscopic Tribology",

Lyon, France, August, 2001.

Presentation at the AFOSR Tribology Program Review, Annapolis, MD,

June, 2002.

VI. Honors/Awards

The 2000 Feynman Nanotechnology Prize (Theory) was awarded to Uzi Landman.

The 2002 Materials Research Society (MRS) Medal was Awarded to Uzi Landman, for pioneering seminal contributions to the field of nanotribology.